

CHEMICAL-CODES:

Chemical Indexing M3 \*01\*

Fragmentation Code

H6 H685 H689 J0 J012 J2 J272 M280 M311 M323

M342 M344 M362 M382 M391 M392 M416 M620 M781 M903

M904 Q454 Q609 Q615 R023

Markush Compounds

199633-B1901-U

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C1996-103536

Non-CPI Secondary Accession Numbers: N1996-275004

PAT-NO: JP408148159A

DOCUMENT-IDENTIFIER: JP 08148159 A

TITLE: NONAQUEOUS ELECTROLYTE

PUBN-DATE: June 7, 1996

INVENTOR-INFORMATION:

NAME

ATA, MASAFUMI

TANAKA, KOICHI

ASSIGNEE-INFORMATION:

NAME

SONY CORP

COUNTRY

N/A

APPL-NO: JP06315527

APPL-DATE: November 24, 1994

INT-CL (IPC): H01M006/16, H01M004/40, H01M004/58, H01M010/40

ABSTRACT:

**PURPOSE:** To provide a nonaqueous electrolyte capable of preventing the precipitation of dendrite at a negative electrode even under an overcharging condition, as a nonaqueous electrolyte useful for a nonaqueous electrolytic battery by adding light metallic salt as the electrolyte as well as the specified compound as a nonaqueous solvent.

**CONSTITUTION:** Light metallic salt is contained as an electrolyte and di-trifluoromethyl malonate contained as a nonaqueous solvent. In this case, di-trifluoromethyl malonate may be used alone, but when other nonaqueous solvents (e.g. propylene carbonate) are used concurrently, the ratio of the malonate is preferably kept equal to or above 10wt.% of the whole solvent. More preferably, the ratio is kept equal to or above 30wt.%. Also, the nonaqueous electrolyte so prepared is applied to a nonaqueous electrolytic battery with a light metal (compound) or preferably a lithium (compound) used as a negative electrode active material.

**COPYRIGHT:** (C)1996,JPO

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平8-148159

(43) 公開日 平成8年(1996)6月7日

(51) Int.Cl. <sup>8</sup>	識別記号	序内整理番号	F I	技術表示箇所
H 0 1 M	6/16	A		
	4/40			
	4/58			
	10/40	A		
		Z		

審査請求 未請求 請求項の数 3 F D (全 5 頁)

(21) 出願番号	特願平6-315527	(71) 出願人	000002185 ソニー株式会社 東京都品川区北品川6丁目7番35号
(22) 出願日	平成6年(1994)11月24日	(72) 発明者	阿多 誠文 東京都品川区北品川6丁目7番35号 ソニー株式会社内
		(72) 発明者	田中 浩一 東京都品川区北品川6丁目7番35号 ソニー株式会社内
		(74) 代理人	弁理士 田沼米 登 (外1名)

(54) 【発明の名称】 非水電解液

(57) 【要約】

【目的】 非水電解液電池において、負極に金属が dendritic 状に析出することが防止し、電池の安全性、信頼性を向上させる。

【構成】 負極が活物質として軽金属又は軽金属化合物を使用する非水電解液電池において、電解質として軽金属塩を含有し、非水溶媒としてジトリフルオロメチルマロネート含有する非水電解液を使用する。

## 【特許請求の範囲】

【請求項1】 電解質として軽金属塩を含有し、非水溶媒としてジトリフルオロメチルマロネートを含有することを特徴とする非水電解液。

【請求項2】 負極活物質として軽金属又は軽金属化合物を使用する非水電解液電池において、非水電解液として請求項1記載の非水電解液を使用する非水電解液電池。

【請求項3】 負極活物質としてリチウム又はリチウム化合物を使用する請求項2記載の非水電解液電池。

## 【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、負極活物質としてリチウム等の軽金属又はその化合物を使用する非水電解液電池のための非水電解液及びその非水電解液を用いた非水電解液電池に関する。

【0002】

【従来の技術】従来より、負極活物質として、リチウム、ナトリウム、アルミニウム等の軽金属を用いた非水電解液電池は、理論上高電圧を発生でき、高エネルギー密度を有するので、民生用電子機器等の電源として期待されている。近年では、そのような非水電解液電池を二次電池化する研究開発が行われており、中でも、リチウム二次電池は、高出力、高エネルギー密度を達成できることから、活発に研究開発が行われている。

【0003】ところで、これらの軽金属を単にそのまま負極に用いた二次電池の場合、充電過程において負極に金属がデンドライト状に析出し、その結果、電池が内部短絡を起こすことが問題となる。そこで、そのようなデンドライト状の金属の析出を防止するため、負極においてこれら軽金属を単にそのまま使用するのではなく、炭素質材料や化合物中にドーパせたり合金化して使用することが提案されている。このような負極によれば電池の安全性や信頼性をある程度高めることができる。

【0004】

【発明が解決しようとする課題】しかしながら、近年、電池の安全性に対する要求が高まり、これまで以上の高度な信頼性が要望されるようになってきている。例えば、電源回路や充電器が故障により、あるいはユーザーの使用方法的誤り等により、電池電圧を上回る高電圧を電池にかけた場合や、通常の充電条件を上回る高電流を電池に流した場合でも、電池が破損せず、安全性が確保されることが求められている。

【0005】本発明は、このような従来技術の課題を解決しようとするものであり、負極活物質として軽金属又は軽金属化合物を使用する非水電解液電池において、負極に軽金属がデンドライト状に析出することを防止し、電池の安全性、信頼性を高めることを目的とする。

【0006】

【課題を解決するための手段】本発明者は、上記の目的

を達成するために鋭意検討した結果、非水電解液を構成する溶媒として、負極活物質とする軽金属のイオンを安定化させることができる特定の溶媒を使用することにより、上記の目的が達成できることを見出し、本発明を完成させるに至った。

【0007】即ち、本発明は、電解質として軽金属塩を含有し、非水溶媒としてジトリフルオロメチルマロネートを含有することを特徴とする非水電解液を提供する。

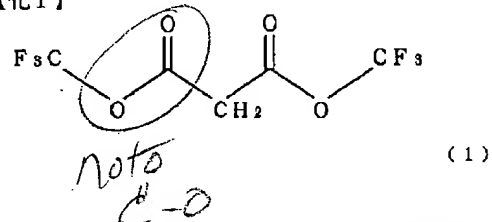
【0008】また、本発明は、負極活物質として軽金属又は軽金属化合物を使用する非水電解液電池において、非水電解液として上記の非水電解液を使用する非水電解液電池を提供する。

【0009】以下、本発明を詳細に説明する。

【0010】本発明の非水電解液は、非水溶媒としてジトリフルオロメチルマロネートを含有することを特徴としている。ジトリフルオロメチルマロネートは次式(1)で表される化合物である。

【0011】

【化1】



このジトリフルオロメチルマロネートは、軽金属イオンと適度に溶媒和して安定化する。したがって、軽金属又は軽金属化合物を負極活物質とする非水電解液電池において、その非水電解液を構成する非水溶媒として、このジトリフルオロメチルマロネートを使用すると、負極に軽金属がデンドライト状に析出することを防止でき、よってデンドライト状に析出した金属により引き起こされる内部短絡も防止することができる。

【0012】本発明の非水電解液は、非水溶媒としてジトリフルオロメチルマロネート単独を使用してもよいが、ジトリフルオロメチルマロネートの他、種々の非水溶媒も含有することができる。例えば、プロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、ビニレンカーボネート、γ-ブチロラクトン、スルホラン、1,2-ジメトキシエタン、1,2-ジエトキシエタン、2-メチルテトラヒドロフラン、3-メチル-1,3-ジオキサラン、プロピオン酸メチル、酪酸メチル、ジメチルカーボネート、ジエチルカーボネート、ジプロピルカーボネート等を使用することができる。特に、電圧に安定な点からプロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、ビニレンカーボネート等の環状カーボネート類、又はジメチルカーボネート、ジエチルカーボネート、ジプロピルカーボネート等の鎖状カーボネート類を使用することが好ましい。また、このような非水溶媒は、1種または2種以上

を組み合わせ使用することができる。

【0013】本発明の非水電解液の非水溶媒を、ジトリフルオロメチルマロネートとその他の非水溶媒との混合溶媒とする場合に、ジトリフルオロメチルマロネートの割合は、電解質の種類等にもよるが、通常、非水溶媒全体の10重量%以上とすることが好ましく、30重量%以上とすることがより好ましい。これによりジトリフルオロメチルマロネートの配合効果を得ることができる。

【0014】一方、本発明の非水電解液を構成する電解質としては、リチウム、ナトリウム、カリウム、セシウム、アルミニウム等の軽金属の塩を使用することができ、当該非水電解液を使用する電池種類等に応じて適宜定めることができる。例えば、非水電解液をリチウム二次電池に使用する場合、電解質としては、 $\text{LiClO}_4$ 、 $\text{LiAsF}_6$ 、 $\text{LiPF}_6$ 、 $\text{LiBF}_4$ 、 $\text{LiCF}_3\text{SO}_3$ 、 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ 等のリチウム塩を使用することができる。このうち特に $\text{LiPF}_6$ や $\text{LiBF}_4$ を使用することが好ましい。

【0015】本発明の非水電解液電池は、負極活物質として軽金属又は軽金属化合物を使用し、非水電解液として上記の非水電解液を使用することを特徴としており、それ以外の構成については従来の種々の非水電解液二次電池あるいは一次電池と同様にすることができる。

【0016】したがって、正極は、目的とする電池の種類に応じて、金属酸化物、金属硫化物又は特定のポリマーを活物質として用いて構成することができる。例えば、リチウム二次電池を構成する場合、正極活物質としては、 $\text{TiS}_2$ 、 $\text{MoS}_2$ 、 $\text{NbSe}_2$ 、 $\text{V}_2\text{O}_5$ 等のリチウムを含有しない金属硫化物あるいは酸化物や、 $\text{Li}_x\text{MO}_2$ （式中、Mは一種以上の遷移金属を表し、通常 $0.05 \leq x \leq 1.10$ である）を主体とするリチウム複合酸化物等を使用することができる。このリチウム複合酸化物を構成する遷移金属Mとしては、Co、Ni、Mn等が好ましい。このようなリチウム複合酸化物の具体例としては、 $\text{LiCoO}_2$ 、 $\text{LiNiO}_2$ 、 $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$ （式中、x、yは電池の充放電状態によって異なり、通常 $0 < x < 1$ 、 $0.7 < y < 1.02$ である）、 $\text{LiMn}_2\text{O}_4$ 等をあげることができる。これらリチウム複合酸化物は、高電圧を発生でき、エネルギー密度的に優れた正極活物質となる。

【0017】正極には、これらの正極活物質の複数種を混合して使用してもよい。また、以上のような正極活物質を使用して正極を形成するに際しては、公知の導電剤や結着材等を添加することができる。

【0018】負極は、その活物質として、軽金属又は軽金属化合物を使用する。このような軽金属としては、リチウム、ナトリウム、カリウム、セシウム、アルミニウム等をあげることができ、特に電池出力やエネルギー密度の点からはリチウムが好ましい。したがって、負極の構成材料としては、このような軽金属又はそのイオンを

ドーブ、脱ドーブできる材料、軽金属、軽金属化合物、軽金属合金を使用することができる。このような負極の構成材料のうちリチウム等の軽金属をドーブ、脱ドーブできる材料としては、例えば、熱分解炭素類、コークス類（ピッチコークス、ニードルコークス、石油コークス等）、グラファイト類、ガラス状炭素類、有機高分子化合物焼成体（フェノール樹脂、フラン樹脂等を適当な温度で焼成し炭素化したもの）、炭素繊維、活性炭等の炭素質材料、あるいはポリアセチレン、ポリピロール等のポリマー等を使用することができる。また、リチウム合金としては、リチウム-アルミニウム合金等を使用することができる。

【0019】このような材料から負極を形成するに際しては、公知の結着材等を添加することができる。

【0020】本発明の電池は、電池形状については特に限定されることはない。円筒型、角型、コイン型、ボタン型等の種々の形状にすることができる。また、一次電池及び二次電池のいずれにも構成することができる。

【0021】

【作用】本発明の非水電解液を使用する本発明の非水電解液電池においては、非水電解液中のジトリフルオロメチルマロネートがラジカルアニオンとなり、負極活物質であるリチウム等の軽金属のイオンとイオンペアを形成し、軽金属イオンを適度に安定化させる。したがって、本発明の電池では、高電圧又は高電流が印加される過充電条件下においても負極でのデンドライトの析出が防止される。よって、本発明の電池は安全性及び信頼性が向上したものとなる。

【0022】

【実施例】以下、図1を参照しつつ、本発明を実施例及び比較例に基づいて具体的に説明する。ここで、図1は、実施例及び比較例で作成した円筒型非水電解液電池の縦半分の断面図である。

【0023】実施例1

（円筒型非水電解液電池の製造）正極1を作製するにあたり、まず、市販の炭酸リチウムと炭酸コバルトとを組成比 $\text{Li}/\text{Co}=1:1$ となるように混合し、空气中900℃で5時間焼成し、リチウム・コバルト酸化物 $\text{LiCoO}_2$ を得た。次に、得られたリチウム・コバルト酸化物を活物質として91重量部、導電剤として黒鉛6重量部、結着剤としてポリフッ化ビニリデン3重量部を混合し、さらにN-メチル-2-ピロリドンで混練し、ペースト状の正極合材を得た。これを帯状のアルミニウム箔の両面に塗布し、帯状の正極を得た。

【0024】一方、負極2を作成するために、まず、粉碎したピッチコークス90重量部に結着剤としてポリフッ化ビニリデン10重量部を混合し、さらにN-メチル-2-ピロリドンで混練し、ペースト状の負極合材を得た。これを帯状の銅箔の両面に塗布し、帯状の負極を得た。

【0025】正極1及び負極2には、集電を行うため、それぞれアルミニウム製の正極リード端子3とニッケル製の負極リード端子4とを溶接した。

【0026】正極1及び負極2の間に、ポリプロピレン製のマイクロポラスフィルムからなるセパレータ5を介在させて積層し、多数回巻回して渦巻型の電極体を作製した。

【0027】この電極体を鉄製電池容器6に収納した。そして負極リード4を電池容器6の内底部にスポット溶接により接続し、正極リード端子3を電池封口板7に同様に接続した。

【0028】一方、炭酸プロピレン(PC)とジトリフルオロメチルマロネートとの体積比1:1の混合溶媒に六フッ化リン酸リチウム1モル/lを溶解させて非水電解液を調製した。そしてこの電解液を電池容器6内に注液し、電池容器6と電池封口板7とをポリプロピレン製パッキング8を介して嵌合してかしめ、密封することにより電池を作製した。

【0029】こうして得られた電池の寸法は、外径20mm、高さ50mmであり、容量は1000mAhであった。

#### 【0030】比較例1

非水電解液として、炭酸プロピレン(PC)と炭酸ジエチルとの体積比1:1の混合溶媒に六フッ化リン酸リチウム1モル/lを溶解させて調製したものを使用する以外は実施例1と同様にして電池を作製した。

#### 【0031】比較例2

非水電解液として、炭酸プロピレン(PC)と1,2-ジメトキシエタンとの体積比1:1の混合溶媒に六フッ化リン酸リチウム1モル/lを溶解させて調製したものを使用する以外は実施例1と同様にして電池を作製した。

#### 【0032】評価

##### (1) 定電流充電試験

実施例及び比較例の電池、各20個ずつについて、3mA/cm<sup>2</sup>の定電流充電試験を行った。この場合、各電池は放電状態で作製されているので、予め、定電圧充電により4.1Vまで充電し、その後定電流充電試験に供した。

【0033】この定電流充電試験は、例えば、充電器の制御回路が故障して急速充電条件のまま過充電状態まで進んだ場合を想定して行ったものであり、この定電流充電試験における電流値は、約1.5C充電に相当している。

【0034】定電流充電試験により電池が使用不能になった事故率と到達電圧の結果を表1に示す。

#### 【0035】

##### 【表1】

	事故率(%)	到達電圧(V)
実施例1	0	6.4
比較例1	70	6.8
比較例2	15	5.0

試験後の電池を分解観察したところ、比較例1の電池では負極表面に多量のリチウムがデンドライト状に析出しているのが確認された。一方、実施例1及び比較例2の電池の負極には、リチウムの析出は見られなかった。

【0036】これにより、比較例1の電池の事故率が高いのは、過充電により負極表面にリチウムがデンドライト状に析出し、これがセパレータを貫通して正極まで到達し、内部短絡を引き起こすためと推定される。

【0037】また、他の実験により、この比較例2の電池の負極の析出リチウムは、非水電解液が電気分解し、その電解質である六フッ化リン酸リチウムのリチウムが電析したものであることがわかった。さらに、六フッ化リン酸リチウムの分解電位は、約6.5V付近であることもわかった。

【0038】したがって、比較例1の電池では到達電位が6.5Vを超えているので六フッ化リン酸リチウムの分解が起こっていることがわかる。これに対して、実施例1及び比較例2の電池では、到達電位が6.5Vに達していないので、六フッ化リン酸リチウムの分解は起こっていないことがわかる。

#### 【0039】(2) 高電圧印加試験

高電圧信頼性を評価するため、実施例及び比較例の各電池20個ずつに7Vの電圧を充電方向に印加し、それによる事故率と電圧印加時に流れた電流値を調べた。なお、この高電圧印加試験は、充電回路の破壊により電池の電圧制御が不能になり、電池に直接高電圧がかかった場合を想定して行ったものである。この結果を表2に示す。

#### 【0040】

##### 【表2】

	事故率(%)	電流値(mA/cm <sup>2</sup> )
実施例1	0	12
比較例1	95	6
比較例2	100	30

試験後の電池を分解観察したところ、比較例1の電池では、負極表面に、定電流充電試験時と同様に多量のリチウムがデンドライト状に析出しているのが確認された。一方、実施例1及び比較例2の電池の負極には、少量のリチウムの析出は認められたが、その析出形態は微粉状であり、デンドライト状ではなかった。

【0041】これにより、比較例1の電池で事故率が高いのは、定電流充電試験時と同様に過充電によるリチウ

ムのデンドライト状の析出による内部短絡が原因と考えられる。

【0042】また、比較例2の電池で事故率が高いのは、非水溶媒として使用した1, 2-ジメトキシエタンの分解電圧が4.6Vと低いため、高電圧の印加により溶媒の分解が急激に進み、多量のガスが発生し、電池を破損させたためと考えられる。

【0043】これに対し、実施例1の電池の負極にはリチウムがデンドライト状に析出しておらず、かつ事故率も低いことから、実施例1で非水溶媒として使用したジトリフルオロメチルマロネートは、リチウムがデンドラ

\*チウム二次電池に使用する非水溶媒として、十分に高い分解電圧を有していることがわかる。

【0044】実施例2～7

非水電解液における炭酸プロピレン(PC)とジトリフルオロメチルマロネートとの体積比を表3のように変える以外は実施例1と同様にして電池を作製し、上記と同様の7V定電圧印加試験に供した。この結果を表3に示す。なお、参考のため、実施例1の結果も表3に合わせて記載した。

【0045】

【表3】

	PC : ジトリフルオロメチルマロネート	リチウム析出状態
実施例2	95 : 5	デンドライト状
実施例3	90 : 10	デンドライト状+微粉状
実施例4	80 : 20	微粉状+小デンドライト状
実施例5	70 : 30	微粉状
実施例1	50 : 50	微粉状
実施例6	30 : 70	微粉状
実施例7	10 : 90	微粉状

表3から、この電池系では、ジトリフルオロメチルマロネートを非水溶媒中に10%以上配合することによりデンドライト抑制効果が現れ、30%以上とすることにより良好にデンドライトの生成を防止できることがわかる。

【0046】なお、ジトリフルオロメチルマロネートと混合する非水溶媒として、炭酸プロピレン(PC)に代えて、炭酸エチレン、炭酸ジエチル等の炭酸エステル及びスルフォラン等の溶媒を使用した場合にも同様にジトリフルオロメチルマロネートの配合割合が10%以上でデンドライト抑制効果が現れた。

【0047】

【発明の効果】非水電解液電池において、本発明の非水電解液を使用すると、負極に金属がデンドライト状に析

※出することが防止される。したがって、電池の安全性、信頼性が大きく向上する。

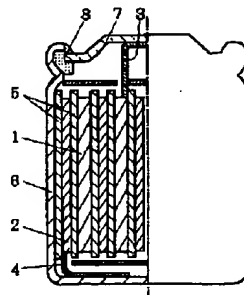
【図面の簡単な説明】

【図1】実施例及び比較例の電池の断面図である。

【符号の説明】

- 1 正極
- 2 負極
- 3 正極リード端子
- 4 負極リード端子
- 5 セパレータ
- 6 電池容器
- 7 電池封口板
- 8 バッキング

【図1】



DERWENT-ACC-NO: 2002-227097

DERWENT-WEEK: 200238

COPYRIGHT 1999 DERWENT INFORMATION LTD

TITLE: New di-(2,2,2-trifluoroethyl) difluoromalonate used as  
solvent in electrolyte, especially for lithium battery

INVENTOR: BOESE, O; KALBREYER, W ; RIELAND, M ; SEFFER, D

PATENT-ASSIGNEE: SOLVAY FLUOR & DERIVATE GMBH[SOLV]

PRIORITY-DATA: 2000DE-1037627 (August 2, 2000)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
WO 200211229 A1	February 7, 2002	G	013	H01M 010/40
AU 200189723 A	February 13, 2002	N/A	000	H01M 010/40
DE 10037627 A1	February 14, 2002	N/A	000	C07C 069/63

DESIGNATED-STATES: AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CO CR CU  
CZ

DK DM DZ EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR  
LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SL TJ  
TM

TR TT TZ UA UG US UZ VN YU ZA ZW AT BE CH CY DE DK EA ES FI FR GB GH GM GR IE  
IT KE LS LU MC MW MZ NL OA PT SD SE SL SZ TR TZ UG ZW

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
WO 200211229A1	N/A	2001WO-EP08478	July 23, 2001
AU 200189723A	N/A	2001AU-0089723	July 23, 2001
AU 200189723A	Based on	WO 200211229	N/A
DE 10037627A1	N/A	2000DE-1037627	August 2, 2000

INT-CL (IPC): C07C067/307, C07C069/63, H01M006/16, H01M010/40

ABSTRACTED-PUB-NO: WO 200211229A

BASIC-ABSTRACT:

NOVELTY - Di-(2,2,2-trifluoroethyl) difluoromalonate (IA) is new.

DETAILED DESCRIPTION - Di-(2,2,2-trifluoroethyl) difluoromalonate (IA) of  
formula (I) is new.



R1, R2 = 2,2,2-trifluoroethyl

INDEPENDENT CLAIMS are also included for:

(a) the use of a wider range of di-(1-4 C)-(fluoro)alkyl difluoromalonates (I) of formula (I);

R1, R2 = 1-4 C alkyl or 1-4 C alkyl with fluorine substituent(s)

) as solvents in electrolytes, especially, of lithium batteries with increased safety;

(b) electrolytes containing (I) and a conductive salt, preferably lithium hexafluorophosphate (LiPF<sub>6</sub>);

(c) mixtures of (I) and other aprotic, non-aqueous electrolyte solvent(s); and

(d) the preparation of (I) by reacting the corresponding dibromomalonate with fluorinating agent, especially potassium fluoride (KF).

USE - (I) are used as solvents in electrolytes, especially of lithium batteries (claimed).

ADVANTAGE - (I) increase the safety of lithium ion batteries, as the flash point of compounds increases with the degree of fluorination.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: NEW DI SOLVENT ELECTROLYTIC LITHIUM BATTERY

DERWENT-CLASS: E16 L03 X16

CPI-CODES: E10-G02B1; E31-K07; L03-E01C2;

EPI-CODES: X16-B01F1; X16-J01C; X16-J08;

CHEMICAL-CODES:

Chemical Indexing M3 \*01\*

Fragmentation Code

H6 H601 H608 H684 H685 H689 J0 J012 J2 J272  
M280 M311 M312 M321 M322 M332 M344 M349 M362 M393  
M416 M620 M710 M720 M781 M782 M904 M905 N209 N225  
N309 N322 N513 Q454 Q615 R023

Specific Compounds

A6PZAM A6PZAN A6PZAP A6PZAU

Chemical Indexing M3 \*02\*

Fragmentation Code

H6 H601 H608 H684 J0 J012 J2 J272 M210 M212  
M272 M282 M311 M321 M344 M349 M362 M391 M416 M620  
M710 M720 M781 M782 M904 M905 N209 N225 N309 N322  
N513 Q454 Q615 R023

Specific Compounds  
A6PZBM A6PZBN A6PZBP A6PZBU

Chemical Indexing M3 \*03\*

Fragmentation Code  
H6 H601 H608 H684 J0 J012 J2 J272 M210 M213  
M232 M272 M282 M311 M321 M344 M349 M362 M391 M416  
M620 M710 M720 M781 M782 M904 M905 N209 N225 N309  
N322 N513 Q454 Q615 R023  
Specific Compounds  
A6PZCM A6PZCN A6PZCP A6PZCU

Chemical Indexing M3 \*04\*

Fragmentation Code  
H6 H601 H608 H684 J0 J012 J2 J272 M210 M213  
M231 M272 M282 M311 M321 M344 M349 M362 M391 M416  
M620 M710 M720 M781 M782 M904 M905 N209 N225 N309  
N322 N513 Q454 Q615 R023  
Specific Compounds  
A6PZDM A6PZDN A6PZDP A6PZDU

Chemical Indexing M3 \*05\*

Fragmentation Code  
H6 H601 H608 H684 J0 J012 J2 J272 M210 M211  
M272 M282 M311 M321 M344 M349 M362 M391 M416 M620  
M710 M720 M781 M782 M904 M905 N209 N225 N309 N322  
N513 Q454 Q615 R023  
Specific Compounds  
A6PZEM A6PZEN A6PZEP A6PZEU

Chemical Indexing M3 \*06\*

Fragmentation Code  
H6 H601 H607 H608 H609 H681 H682 H683 H684 H685  
H689 J0 J012 J2 J272 M210 M211 M212 M213 M214  
M215 M216 M231 M232 M233 M272 M280 M281 M282 M311  
M312 M313 M314 M315 M321 M322 M323 M331 M332 M333  
M334 M340 M342 M343 M344 M349 M362 M391 M392 M393  
M416 M620 M710 M720 M781 M782 M904 M905 N209 N225  
N309 N322 N513 Q454 Q615 R023  
Markush Compounds  
200060-02101-M 200060-02101-N 200060-02101-P 200060-02101-U

Chemical Indexing M3 \*07\*

Fragmentation Code  
A103 A940 B115 B720 B752 B819 B831 C009 C100 C803  
C804 C805 C806 C807 M411 M782 M904 M905 Q454 R023  
Specific Compounds  
10929K 10929M

Chemical Indexing M3 \*08\*

Fragmentation Code  
H6 H603 H608 H684 J0 J012 J2 J272 M210 M212

M272 M282 M311 M321 M344 M349 M362 M391 M416 M620  
M730 M904 M905  
Specific Compounds  
A6Q0AK A6Q0AS

Chemical Indexing M3 \*09\*

Fragmentation Code  
A119 A940 C009 C100 C730 C801 C803 C804 C805 C806  
C807 M411 M730 M904 M905 M910  
Specific Compounds  
01815K 01815S  
Registry Numbers  
1815S 1815U

UNLINKED-DERWENT-REGISTRY-NUMBERS: 1815S; 1815U

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C2002-069138  
Non-CPI Secondary Accession Numbers: N2002-174308

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum  
Internationales Büro



(43) Internationales Veröffentlichungsdatum  
7. Februar 2002 (07.02.2002)

PCT

(10) Internationale Veröffentlichungsnummer  
WO 02/11229 A1

- (51) Internationale Patentklassifikation<sup>7</sup>: **H01M 10/40**, C07C 67/307
- (21) Internationales Aktenzeichen: PCT/EP01/08478
- (22) Internationales Anmeldedatum:  
23. Juli 2001 (23.07.2001)
- (25) Einreichungssprache: Deutsch
- (26) Veröffentlichungssprache: Deutsch
- (30) Angaben zur Priorität:  
100 37 627.4 2. August 2000 (02.08.2000) DE
- (81) Bestimmungsstaaten (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Bestimmungsstaaten (*regional*): ARIPO-Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Anmelder (*für alle Bestimmungsstaaten mit Ausnahme von US*): SOLVAY FLUOR UND DERIVATIVE GMBH [DE/DE]; Hans-Böckler-Allee 20, 30173 Hannover (DE).
- (72) Erfinder; und
- (75) Erfinder/Anmelder (*nur für US*): BÖSE, Olaf [DE/DE]; Ritter-Brünning-Strasse 26, 30449 Hannover (DE). RIELAND, Matthias [DE/DE]; Königsberger Ring 41 A, 30559 Hannover (DE). SEFFER, Dirk [DE/DE]; Boelckestrasse 14, 31535 Neustadt (DE). KALBREYER, Wolfgang [DE/DE]; Wellie 12, 31595 Steyerberg (DE).
- (74) Anwalt: FISCHER, Reiner; Solvay Pharmaceuticals GmbH, Hans-Böckler-Allee 20, 30173 Hannover (DE).
- Veröffentlicht:**  
— mit internationalem Recherchenbericht  
— vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen
- Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.*



WO 02/11229 A1

(54) Title: NOVEL USE OF DIFLUOROMALONIC ACID ESTERS

(54) Bezeichnung: NEUARTIGE VERWENDUNG VON DIFLUORMALONSÄUREESTERN

(57) Abstract: Difluoromalonic acid dialkyl esters can be used as solvents in electrolytes for lithium-ion batteries. The invention also relates to novel compounds of difluoromalonic acid.

(57) Zusammenfassung: Difluormalonsäuredialkylester können als Lösemittel in Elektrolyten für Lithiumionen-Batterien verwendet werden. Beschrieben werden auch neue Verbindungen der Difluormalonsäure.

## Neuartige Verwendung von Difluormalonsäureestern

## Beschreibung

Die Erfindung bezieht sich auf eine neuartige Verwendungsmöglichkeit für Difluormalonsäureester und eine neue Verbindung.

Lithiumionen-Batterien weisen einen Elektrolyten auf, der ein Leitsalz umfaßt sowie ein oder mehrere polare, aprotische Lösungsmittel. Ein sehr gutes Leitsalz ist  $\text{LiPF}_6$ . Andere brauchbare Lithiumsalze sind  $\text{LiBF}_4$ , das Lithiumsalz der Trifluormethansulfonsäure, die Lithiumsalze von Bis-trifluormethansulfonyl)imiden oder Lithiumsalze von Verbindungen des sechsfach koordinierten Phosphors mit F und  $\text{CF}_3$ -Gruppen als Substituent, wie in der WO 98/15562 angegeben. Als Lösungsmittel werden beispielsweise Alkylencarbonate, acyclische Carbonate, Ether, Formamide, Sulfolane oder Methylsulfolane eingesetzt. Brauchbar sind auch bestimmte Nitrile oder stickstoffhaltige Verbindungen, wie Nitromethan, Pyrrolidione etc. siehe z. B. Macoto Ue, Kazuhiko Ida, und Shoichiro Mori in J. Electrochem. Soc. 141 (1994), Seiten 2989 - 2996.

Aufgabe der vorliegenden Erfindung war es, weitere, als Lösungsmittel für Elektrolyte verwendbare Verbindungen anzugeben, die zu einer erhöhten Sicherheit der Lithiumionen-batterie beitragen können. Diese Aufgabe wird durch die Erfindung gelöst. Erfindungsgemäß werden Verbindungen der allgemeinen Formel (I)  $\text{R}^1\text{-O-C(O)-CF}_2\text{-C(O)-O-R}^2$ , worin  $\text{R}^1$  und  $\text{R}^2$  gleich oder verschieden sind und für C1-C4-Alkyl oder für durch mindestens 1 Fluoratom substituiertes C1-C4-Alkyl stehen, als Lösungsmittel in Elektrolyten, insbesondere von Lithiumionen-Batterien.

Bevorzugt sind  $R^1$  und  $R^2$  gleich. Besonders bevorzugt bedeuten sie Methyl, Ethyl, n-Propyl, i-Propyl oder 2,2,2-Trifluorethyl.

Die Verbindungen der Formel (I) können als alleiniges Lösungsmittel in Elektrolyten verwendet werden. Bevorzugt wird eine Verbindung der Formel (I) zusammen mit mindestens einem weiteren polaren, aprotischen organischen Lösungsmittel eingesetzt. Als weiteres Lösungsmittel können die bereits bekannten Lösungsmittel für Elektrolyte verwendet werden. Brauchbare Lösungsmitteltypen sind beispielsweise in der angegebenen Literaturstelle von Ue et al. erwähnt. Besonders gut brauchbar sind Dialkylcarbonate, Alkylencarbonate, Lactone, Nitrile und Formamide. Gut brauchbar sind Gemische mit den, in der WO 00/38264 offenbarten, alkylenverbrückten Diestern. Sehr vorteilhaft sind auch Gemische mit Dialkylamiden von fluorierten Carbonsäuren, beispielsweise von N,N-Dialkylamiden der Trifluoressigsäure, die z. B. in der WO 00/38259 offenbart sind. "Alkyl" steht hier vorzugsweise für C1-C4-Alkyl. Das Mol-Verhältnis der Verbindung der Formel (I) und des anderen Lösungsmittels liegt bevorzugt im Bereich von 1:0,5 bis 1:10. Neben solchen Lösungsmittelgemischen sind Elektrolyte, die eine Verbindung der allgemeinen Formel (I) und ein Leitsalz sowie gegebenenfalls weitere bekannte Elektrolytlösungsmittel enthalten, ebenfalls Gegenstand der Erfindung. Bevorzugte Leitsalze umfassen als Kation das Lithium-Kation. Bevorzugtes Anion des Leitsalzes ist das einfach negativ geladene Anion  $PF_6$ , brauchbar sind aber auch die einfach negativ geladenen Anionen  $BF_4$ ,  $CF_3SO_3$ ,  $ClO_4$ ,  $[N(SO_2CF_3)_2]$  oder  $PF_x(CF_3)_y$ , worin  $x + y = 6$  gilt und  $x = 1$  bis 5 und  $y = 1$  bis 5 ist. Bevorzugt ist im erfindungsgemäßen Elektroyten zusätzlich zu einer oder mehreren Verbindungen der Formel (I) ein weiteres Elektrolytlösungsmittel enthalten, vorzugsweise ein Dialkylcarbonat, ein Alkylencarbonat oder ein N,N-Dialkylamid der Trifluoressigsäure, wobei Alkyl für C1-C4-Alkyl, steht. Brauchbar sind als weiteres Elektrolytlösungsmittel auch Amide der Trifluoressigsäure, in wel-

chen der Amid-Stickstoff in ein 5- oder 6-Ringsystem eingebaut ist, welches auch Heteroatome wie Sauerstoff enthalten kann. Beispiele sind Amide der Trifluoressigsäure, in welchen die Amidgruppe durch die Pyrrolidinyl-, Morpholinyl- oder Piperidinyl-Gruppe gebildet ist.

$\text{CF}_3\text{CH}_2\text{-O-C(O)CF}_2\text{C(O)-O-CH}_2\text{CF}_3$  ist neu und ebenfalls Gegenstand der Erfindung.

Die Herstellung von Difluormalonestern aus den entsprechenden Chlorverbindungen und Aminfluorid-HF-Addukten offenbart die EP-A 597 329.

Zur Herstellung der Verbindungen der Formel (I) kann man ausgehen von analogen Verbindungen der Formel  $\text{R}^1\text{-O-C(O)-CBr}_2\text{-C(O)-O-R}^2$ . Ester mit  $\text{R}^1, \text{R}^2 = \text{Methyl oder Ethyl}$  sind z. B. im Handel erhältlich. Andere Ester erhält man durch Umesterung (vor oder nach der Fluorierung). Die Ausgangsverbindung setzt man mit einem Fluorierungsmittel wie KF um. Ein geeignetes Lösungsmittel wie Sulfolan kann eingesetzt werden. Dieses Verfahren ist neu und ebenfalls Gegenstand der Erfindung.

Ein anderes Herstellungsverfahren durch alkalische Permanganat-Oxidation von Polyfluorocyclohexenen offenbaren E. J. P. Fear et al. in J. Appl. Chem. 5 (1955), Seiten 589 - 594. Eine weitere Herstellungsmethode umfaßt die Fluorierung des Monobromderivates der jeweiligen Malonester, siehe E. D. Bergmann et al. in J. Chem. Soc. 1959, Seiten 3286 - 3289.

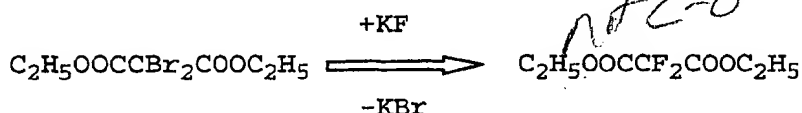
Die Technik, insbesondere im Hinblick auf die Palette der verfügbaren Lösungsmittel, besonders bei Elektrolyten für Batterien wird durch die Erfindung bereichert. Die Verbindungen weisen durch ihren Fluorierungsgrad einen erhöhten Flammpunkt auf und tragen dadurch zu einer erhöhten Sicherheit der Lithiumionenbatterie bei.

Die folgenden Beispiele sollen die Erfindung weiter erläutern, ohne sie in ihrem Umfang einzuschränken.

### Beispiele

#### Beispiel 1:

Herstellung von Difluormalonsäurediethylester



In einem 2 l Kolben mit Rückflußkühler und Rührer wurden Dibrommalonsäurediethylester (318 g; 1 mol; 318 g mol<sup>-1</sup>), Kaliumfluorid (232 g; 4 mol; 58 g mol<sup>-1</sup>) und 250 ml Sulfolan vorgelegt. Das Reaktionsgemisch wurde auf 80 bis 150 °C erwärmt. Nach dem Abkühlen wurde dreimal mit je 40 ml Dichlormethan extrahiert. Das erhaltene Rohprodukt wurde destillativ gereinigt.

Ausbeute: 81,2 g (0,472 mol, 172 g mol<sup>-1</sup>; 47,2 %)

Kp.: 66 - 68 °C bei 10 mbar

<sup>1</sup>H-NMR: 1,36 ppm (Triplett, CH<sub>3</sub>); 4,39 ppm (Quartett, CH<sub>2</sub>)

<sup>12</sup>C-NMR: 13,79 ppm (Singulett, CH<sub>3</sub>); 63,91 ppm (Singulett, CH<sub>2</sub>); 106,24 ppm (Triplett, CF<sub>2</sub>); 160,85 ppm (Triplett, CO)

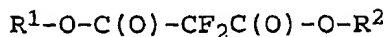
<sup>19</sup>F-NMR: Singulett, CF<sub>2</sub>

Die Löslichkeit an Li[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] betrug mehr als 2 mol/l.



## Patentansprüche

1. Verwendung von Verbindungen der allgemeinen Formel (I)



worin  $R^1$  und  $R^2$  gleich oder verschieden sind und für C1-C4-Alkyl oder für durch mindestens 1 Fluoratom substituiertes C1-C4-Alkyl stehen, als Lösungsmittel in Elektrolyten, insbesondere von Lithium-Batterien mit erhöhter Sicherheit.

2. Verwendung nach Anspruch 1, wobei  $R^1$  und  $R^2$  gleich sind und Methyl, Ethyl, i-Propyl, n-Propyl oder 2,2,2-Trifluorethyl bedeuten.

3. Verwendung nach Anspruch 1, dadurch gekennzeichnet, daß mindestens ein weiteres, aprotisches, nichtwäßriges Elektrolytlösungsmittel eingesetzt wird.

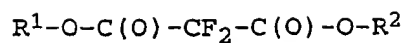
4. Verbindung der allgemeinen Formel (I), worin  $R^1$  und  $R^2$  2,2,2-Trifluorethyl bedeuten.

5. Elektrolyt, umfassend eine Verbindung der allgemeinen Formel (I) und ein Leitsalz, vorzugsweise  $LiPF_6$ .

6. Elektrolyt, weiterhin umfassend mindestens ein weiteres aprotisches, nichtwäßriges Elektrolytlösungsmittel.

7. Gemische, umfassend Verbindungen der Formel (I) und mindestens ein weiteres Elektrolytlösungsmittel.

8. Verfahren zur Herstellung von Verbindungen der Formel (I)



worin  $R^1$  und  $R^2$  die oben angegebene Bedeutung besitzen,  
durch Umsetzung von Verbindungen der Formel (Ia)



mit Fluorierungsmitteln, insbesondere KF.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/08478

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 H01M10/40 C07C67/307

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, BEILSTEIN Data, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 948 073 A (DAIKIN IND LTD) 6 October 1999 (1999-10-06) page 3, line 32 -page 4, line 33 page 5, line 10-53 page 7; table 1 page 10, line 9-25 page 11, line 18-26; claims 1-5	1-7
X	WO 00 01027 A (DURACELL INC) 6 January 2000 (2000-01-06) page 1, line 18 -page 2, line 10 page 2, line 30 -page 4, line 15; claim 1 --- -/--	1-3,5-7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

12 December 2001

Date of mailing of the international search report

28/12/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

De Vos, L

## INTERNATIONAL SEARCH REPORT

International Application No

PCI/EP 01/08478

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 11, 29 November 1996 (1996-11-29) & JP 08 190932 A (NIPPON TELEGR &AMP;TELEPH CORP &LT;NTT&GT;), 23 July 1996 (1996-07-23) abstract ---	1-7
A	DATABASE WPI Section Ch, Week 199350 Derwent Publications Ltd., London, GB; Class C03, AN 1993-400364 XP002185482 & JP 05 301844 A (IDEMITSU KOSAN CO LTD), 16 November 1993 (1993-11-16) abstract ---	8
A	EP 0 005 810 A (HOECHST AG) 12 December 1979 (1979-12-12) page 2, line 17 -page 3, line 3 page 4, line 6-35; claims 1-6 ---	8
A	EP 0 597 329 A (BAYER AG) 18 May 1994 (1994-05-18) cited in the application page 2, line 20 -page 3, line 42 page 5; claims 1-10; example 3 -----	8

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/08478

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0948073	A	06-10-1999	JP 11007978 A	12-01-1999
			EP 0948073 A1	06-10-1999
			CN 1229529 T	22-09-1999
			WO 9857385 A1	17-12-1998
			TW 391071 B	21-05-2000
			US 6174628 B1	16-01-2001
WO 0001027	A	06-01-2000	US 6045950 A	04-04-2000
			AU 4433599 A	17-01-2000
			WO 0001027 A1	06-01-2000
JP 08190932	A	23-07-1996	NONE	
JP 5301844	A	16-11-1993	NONE	
EP 0005810	A	12-12-1979	DE 2823969 A1	13-12-1979
			DE 2960046 D1	05-02-1981
			EP 0005810 A1	12-12-1979
			JP 54157503 A	12-12-1979
EP 0597329	A	18-05-1994	DE 4237882 A1	11-05-1994
			DE 59305389 D1	20-03-1997
			EP 0597329 A2	18-05-1994
			JP 6219987 A	09-08-1994
			US 5391811 A	21-02-1995

# INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen

PC 1/EP 01/08478

**A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES**  
IPK 7 H01M10/40 C07C67/307

Nach der internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

## B. RECHERCHIERTE GEBIETE

Recherchierte Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)  
IPK 7 H01M C07C

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

EPO-Internal, PAJ, BEILSTEIN Data, WPI Data

## C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	EP 0 948 073 A (DAIKIN IND LTD) 6. Oktober 1999 (1999-10-06) Seite 3, Zeile 32 -Seite 4, Zeile 33 Seite 5, Zeile 10-53 Seite 7; Tabelle 1 Seite 10, Zeile 9-25 Seite 11, Zeile 18-26; Ansprüche 1-5 ---	1-7
X	WO 00 01027 A (DURACELL INC) 6. Januar 2000 (2000-01-06) Seite 1, Zeile 18 -Seite 2, Zeile 10 Seite 2, Zeile 30 -Seite 4, Zeile 15; Anspruch 1 --- -/--	1-3,5-7

☒ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

☒ Siehe Anhang Patentfamilie

\* Besondere Kategorien von angegebenen Veröffentlichungen :

\*A\* Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist

\*E\* älteres Dokument, das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist

\*L\* Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt)

\*O\* Veröffentlichung, die sich auf eine mündliche Offenbarung, eine Benutzung, eine Ausstellung oder andere Maßnahmen bezieht

\*P\* Veröffentlichung, die vor dem internationalen Anmeldedatum, aber nach dem beanspruchten Prioritätsdatum veröffentlicht worden ist

\*T\* Spätere Veröffentlichung, die nach dem internationalen Anmeldedatum oder dem Prioritätsdatum veröffentlicht worden ist und mit der Anmeldung nicht kollidiert, sondern nur zum Verständnis des der Erfindung zugrundeliegenden Prinzips oder der ihr zugrundeliegenden Theorie angegeben ist

\*X\* Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann allein aufgrund dieser Veröffentlichung nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden

\*Y\* Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist

\*G\* Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche

12. Dezember 2001

Absenddatum des internationalen Recherchenberichts

28/12/2001

Name und Postanschrift der Internationalen Recherchenbehörde  
Europäisches Patentamt, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Bevollmächtigter Bediensteter

De Vos, L

## INTERNATIONALER RECHERCHENBERICHT

Intel nales Aktenzeichen

PCI/EP 01/08478

C.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN		
Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Beitr. Anspruch Nr.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 1996, no. 11, 29. November 1996 (1996-11-29) &amp; JP 08 190932 A (NIPPON TELEGR &amp;AMP;TELEPH CORP &amp;LT;NTT&amp;GT;), 23. Juli 1996 (1996-07-23) Zusammenfassung</p> <p>---</p>	1-7
A	<p>DATABASE WPI Section Ch, Week 199350 Derwent Publications Ltd., London, GB; Class C03, AN 1993-400364 XP002185482 &amp; JP 05 301844 A (IDEMITSU KOSAN CO LTD), 16. November 1993 (1993-11-16) Zusammenfassung</p> <p>---</p>	8
A	<p>EP 0 005 810 A (HOECHST AG) 12. Dezember 1979 (1979-12-12) Seite 2, Zeile 17 -Seite 3, Zeile 3 Seite 4, Zeile 6-35; Ansprüche 1-6</p> <p>---</p>	8
A	<p>EP 0 597 329 A (BAYER AG) 18. Mai 1994 (1994-05-18) in der Anmeldung erwähnt Seite 2, Zeile 20 -Seite 3, Zeile 42 Seite 5; Ansprüche 1-10; Beispiel 3</p> <p>-----</p>	8

# INTERNATIONALER RECHERCHENBERICHT

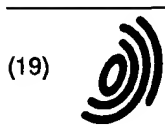
Angaben zu Veröffentlichung die zur selben Patentfamilie gehören

Internationales Aktenzeichen

PCT/EP 01/08478

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
EP 0948073 A	06-10-1999	JP 11007978 A	12-01-1999
		EP 0948073 A1	06-10-1999
		CN 1229529 T	22-09-1999
		WO 9857385 A1	17-12-1998
		TW 391071 B	21-05-2000
		US 6174628 B1	16-01-2001
WO 0001027 A	06-01-2000	US 6045950 A	04-04-2000
		AU 4433599 A	17-01-2000
		WO 0001027 A1	06-01-2000
JP 08190932 A	23-07-1996	KEINE	
JP 5301844 A	16-11-1993	KEINE	
EP 0005810 A	12-12-1979	DE 2823969 A1	13-12-1979
		DE 2960046 D1	05-02-1981
		EP 0005810 A1	12-12-1979
		JP 54157503 A	12-12-1979
EP 0597329 A	18-05-1994	DE 4237882 A1	11-05-1994
		DE 59305389 D1	20-03-1997
		EP 0597329 A2	18-05-1994
		JP 6219987 A	09-08-1994
		US 5391811 A	21-02-1995





Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 0 806 804 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:  
12.11.1997 Bulletin 1997/46

(51) Int. Cl.<sup>6</sup>: H01M 10/40

(21) Application number: 97107475.2

(22) Date of filing: 06.05.1997

(84) Designated Contracting States:  
DE FR GB

(30) Priority: 11.05.1996 JP 152832/96

(71) Applicant:  
FURUKAWA DENCHI KABUSHIKI KAISHA  
Yokohama-shi, Kanagawa-ken (JP)

(72) Inventors:  
• Sakai, Shigeru  
c/o Iwaki Jigyosho  
Shimofunao-machi, Iwaki-shi (JP)

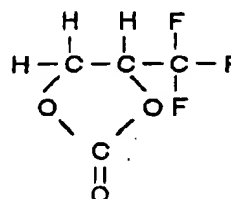
• Yamamoto, Masahiro  
c/o Iwaki Jigyosho  
Shimofunao-machi, Iwaki-shi (JP)

(74) Representative:  
Schmidt-Evers, Jürgen, Dipl.-Ing. et al  
Patentanwälte Mitscherlich & Partner,  
Sonnenstrasse 33  
80331 München (DE)

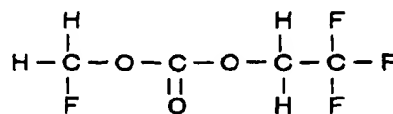
(54) Fluorinated carbonate electrolytes for use in a lithium secondary battery

(57) A lithium secondary battery comprising a negative electrode using as an active material at least one kind selected from the group of metallic lithium, lithium alloys or materials which are capable of electrochemically occluding and releasing lithium ions, a positive electrode using as an active material at least one kind of compounds which are capable of electrochemically occluding and releasing lithium ions, and an organic electrolyte. It is characterized in that a solvent for the organic electrolyte is composed mainly of a mixture solvent prepared by mixing an organic solvent indicated by structure expression I, i.e. 4-trifluoromethyl-1,3-dioxolane-2-one, with one kind selected from the group of organic solvent indicated by structure expression II, e.i. 1-trifluoroethylmethyl carbonate, and/or an organic solvent indicated by structure expression III, i.e. di-1-trifluoroethyl carbonate, as mentioned below. As a result of using the solvent which contains the above-mentioned mixture solvent as a main component for the electrolyte, a lithium secondary battery with improved high-rate discharge characteristics, cycle characteristics and safety characteristics is obtained.

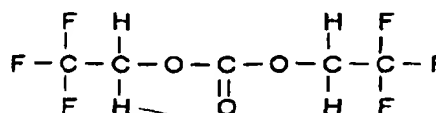
Structure expression I



Structure expression II



Structure expression III



EP 0 806 804 A1

## Description

## FIELD OF THE INVENTION

This invention relates to a lithium secondary battery

## BACKGROUND OF THE INVENTION

With recent rapid progress in the field of the electric and electronic industries, electric and electronic devices have been made higher in performance, smaller in size and portable. As such, the development of these devices has generated considerable demand for secondary batteries with high energy density which can be used for these electronic devices.

As a secondary battery to be used for these electronic devices, lead acid batteries, Ni-Cd (nickel-cadmium) batteries or Ni-MH (nickel-hydrogen) batteries have been conventionally used. In addition to them, lithium secondary batteries which use metallic lithium or carbon material capable of electro-chemically occluding and releasing lithium ions as an active material of a negative electrode, and oxide materials containing lithium capable of electro-chemically occluding and releasing lithium ions as an active material of a positive electrode, have been put into practice and widely used recently.

Lithium secondary batteries of this kind have, as compared with other conventional batteries, high discharge voltage and high energy density per unit volume or unit weight. Therefore it is said that they are the most promising secondary batteries today.

Presently, as an electrolyte used in this kind of lithium secondary batteries, there has been used such a one that lithium salt such as  $\text{LiPF}_6$ , etc. is dissolved in a non-aqueous mixture solvent wherein the main component is a mixture solvent of an organic solvent such as propylene carbonate, etc., which has dielectric constant, and an organic solvent such as methyl ethyl carbonate, etc., which has low viscosity. (see Tokkai-Hei 6-13109)

However, this kind of lithium secondary battery has such a problem that the organic solvents in the electrolyte is decomposed during charging, and the battery capacity is decreased by repetition of charge-discharged cycles. Therefore, the improvement in the length of battery life has been desired.

Also, since these conventional electrolytes are combustible, the lithium secondary battery using this kind of electrolyte has such dangers as firing or explosion when it is mishandled, as compared with such batteries using the aqueous electrolyte such as lead acid, Ni-Cd battery or Ni-MH battery.

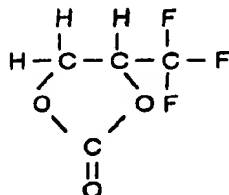
## SUMMARY OF THE INVENTION

An object of the present invention is to provide a lithium secondary battery which has equal or higher high-rate discharge characteristics and more excellent cycle characteristics than the conventional lithium secondary battery using the conventionally proposed electrolytes, by using an organic electrolyte including a mixture solvent which is more stable chemically and electrically as compared with the conventional electrolytes.

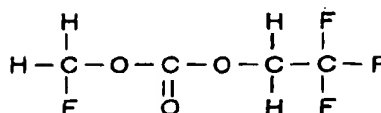
Another object of the present invention is to provide a lithium secondary battery which has, in addition to the excellent cycle life characteristics, a self-extinguishing characteristics of the electrolyte and is excellent in safety by limiting the electrolyte to the specific range.

To achieve one object of the present invention among the above-mentioned objects, according to the present invention, a lithium secondary battery is characterized in that a solvent for the organic electrolyte is composed mainly of a mixture solvent prepared by mixing an organic solvent indicated by structure expression I, i.e. 4-trifluoromethyl-1,3-dioxolane-2-one, and one kind or two selected from the group of organic solvents indicated by structure expression II, i.e. 1-trifluoroethylmethyl carbonate, and an organic solvent indicated by structure expression III, i.e. di-1-trifluoroethyl carbonate.

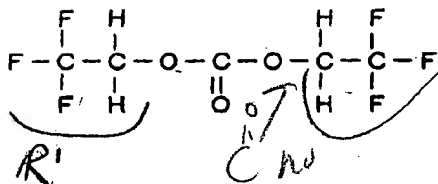
Structure expression I



Structure expression II



Structure expression III



To achieve the foregoing another object of the present invention, according to the present invention, a lithium secondary battery is characterized in that the volume rate of the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of organic solvents indicated by structure expression II and structure expression III occupied in the whole solvent for the organic electrolyte is 65% or more when measured under environmental temperature of 25°C, and that the volume rate of the organic solvent indicated by structure expression I occupied in the mixture solvent is 35 % or more when measured under environmental temperature of 25°C, and thereby there is offered the organic electrolyte having excellent self-extinguishing and safe characteristics in addition to the excellent cycle characteristics of the battery.

Also, a lithium secondary battery, according to the present invention is characterized in that the volume rate of the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of organic solvents indicated by structure expression II and structure expression III which are occupied in the whole solvent for the organic electrolyte is 80% or more when measured under environmental temperature of 25°C, and thereby there is offered the battery which is particularly good in cycle characteristics.

And also, a lithium secondary battery, according to the present invention is characterized in that the volume rate of the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of organic solvents indicated by structure expression II and structure expression III occupied in the whole solvent for the organic electrolyte is 80% or more when measured under environmental temperature of 25°C, and that the volume rate of the organic solvent indicated by structure expression I occupied in the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of organic solvents indicated by structure expression II and structure expression III is 35-65 % when measured under environmental temperature of 25°C, and thereby there is offered one of the most preferable batteries which is particularly good in high-rate discharge characteristics and cycle characteristics and is excellent in safety.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred embodiments of the present invention will be described in details as follows.

A lithium secondary battery according to the present invention makes no differences from conventional lithium secondary batteries in constructional parts except for using an organic electrolyte prepared by dissolving at least one kind of lithium salts in a whole solvent has higher chemical and electrical stability than the conventional electrolytes.

Here, the whole solvent which has higher stability chemically and electrically than the conventional electrolytes is mainly composed of the above-mentioned mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure expression II and structure expression III.

As for a solvent with high dielectric constant to be selectively used here, it is important that the solvent itself is high in chemically and electrically stable, but it is more important that the resultant mixture solvent prepared by mixing it with any other kind of solvent is also high in the above-mentioned stability. As a result of various and many investigations, it has been found that there is brought about excellent cycle characteristics when the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure expression II and structure expression III is used.

Specific actions for offering the foregoing excellent cycle characteristics are unknown, but it is presumed that it is due to the fact that the organic solvent itself indicated by structure expression I has the high chemical and electrical stability and also due to the interactions between the organic solvent indicated by structure expression I and one kind or two selected from the group of the organic solvent indicated by structure expression II and the organic solvent indicated by structure expression III as resulted from the mixture thereof.

Thus, if the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure expression II and structure expression III is present as a main component in the whole organic solvent for the electrolyte, there is brought about the excellent cycle characteristics. In that case, the inventors have found that if the volume rate of the mixture solvent occupied in the whole solvent for the organic electrolyte is 65% or more when measured under environmental temperature of 25°C and the volume rate of the organic solvent indicated by structure expression I occupied in the mixture solvent is 35% or more when measured under environmental temperature of 25°C, there can be provided a lithium secondary battery which has self-extinguishing characteristics of the electrolyte and is excellent in safety, in addition to the excellent cycle characteristics. These characteristic features are presumed to be due to the interactions between the respective solvents resulted from mixing the organic solvent indicated by structure expression I and one kind or two selected from the group of the organic solvents indicated by structure expression II and structure expression III.

Thus, if the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure expression II and structure expression III is present as a main component for the whole solvent, there can be an excellent cycle characteristics. Furthermore, the inventors also have found that if the volume rate of the mixture solvent occupied in the whole solvent for the organic electrolyte is 80 % or more when measured under environmental temperature of 25°C, there can be obtained a lithium secondary battery which is especially excellent in cycle characteristics. The inventors assume that the reason for this is because the actions (influence(s)) of other solvent(s) than the solvents indicated by structure expressions I, II and III are hardly presented under environmental temperature of 25°C if the volume rate of the mixture solvent in the whole solvent is 80 % or more.

Here, solvents used in the electrolyte other than the solvents indicated by structure expressions I, II and III can be, for example, cyclic esters such as propylene carbonate, ethylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone, vinylene carbonate, 2-methyl- $\gamma$ -butyrolactone, acetyl- $\gamma$ -butyrolactone and  $\gamma$ -valerolactone, chain esters such as dimethyl carbonate, methyl ethyl carbonate, propyl methyl carbonate, methyl butyl carbonate, diethyl carbonate, propyl ethyl carbonate, ethyl butyl carbonate, dipropyl carbonate, butyl propyl carbonate, dibutyl carbonate, alkyl propionates ester, dialkyl malonates ester and alkyl acetate ester, cyclic ethers such as alkyl acetates, tetrahydrofuran, alkyl tetrahydrofuran, dialkyl tetrahydrofuran, alkoxy tetrahydrofuran, dialkoxy tetrahydrofuran, 1,3-dioxolane, alkyl-1,3-dioxolane, 1,4-dioxolane, etc. and chain ethers such as 1,2-dimethoxyethane, 1,2-diethoxyethane, diethyl ether, ethylene glycol dialkyl ether, diethylene glycol dialkyl ether, triethylene glycol dialkyl ether and tetraethylene glycol dialkyl ether. However, it is not necessary to be limited to the solvents as listed above.

Thus, if the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure expression II and structure expression III is present in the whole solvent as main component, there is brought about an excellent characteristics. Further, the inventors have also found that it is preferable that the volume rate of the mixture solvent occupied in the whole solvent for the organic electrolyte is 80 % or more when measured under environmental temperature of 25°C, and the volume rate of the organic solvent indicated by structure expression I occupied in the mixture solvent is 35-65 % when measured under environmental temperature condition of 25°C. More in detail, the inventors have found that especially when the volume rate of the organic solvent indicated by structure expression I is limited in the above range, there can be obtained a lithium secondary battery which has an especially high specific electric conductivity, and thus there can be obtained a large discharge capacity even if it is discharged with a current in a wide range of 0.2CA - 2.5CA, in addition to the especially excellent cycle characteristics and a high safety resulted from the self-extinguishing characteristics of

the electrolyte. And, if the foregoing volume rate of the organic solvent indicated by structure expression I is less than 35%, the lithium salt can not be dissociated sufficiently, resulting in decrease in the specific electric conductivity and increase in the internal resistance of the battery, so that it becomes difficult to take out a sufficient capacity. On the other hand, if the volume rate thereof is more than 65%, the viscosity of the electrolyte is increased, resulting in decrease in mobility of lithium ions and decrease in the specific conductivity and increase in the internal resistance.

As to lithium salts to be dissolved in the whole solvent for the electrolyte, any kind which is capable of dissociating in the organic solvent and releasing lithium ions can be used. For example, there are inorganic lithium salt such as  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiCl}$ ,  $\text{LiBr}$  etc., and organic lithium salt such as  $\text{LiB}(\text{C}_6\text{H}_5)_4$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ ,  $\text{LiOSO}_2\text{CF}_3$  etc.. Among the above lithium salts, fluorine-containing lithium salts are preferable in terms of safety, and especially  $\text{LiPF}_6$  alone or a mixture composed mainly of  $\text{LiPF}_6$  mixed with any other lithium salt(s) are preferable because of its high electro-conductivity.

The active materials to be used for the positive electrode are, for example, lithium-containing complex oxides such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMnO}_2$  or  $\text{LiMn}_2\text{O}_4$ , etc., or chalcogen compounds such as  $\text{TiO}_2$ ,  $\text{MnO}_2$ ,  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{TiS}_2$ ,  $\text{MoS}_2$ , etc.. Specially, a lithium compound having a structure of  $\alpha\text{-NaCrO}_2$  such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMnO}_2$  etc. or  $\text{LiMn}_2\text{O}_4$  etc. are more preferable because of its high discharge voltage and electro-chemical stability.

### EMBODIMENT EXAMPLES

The embodiment examples of the present invention will be explained concretely as follows, but the present invention is not to limit to them.

$\text{LiCoO}_2$  powder as an active material for a positive electrode, graphite powder as an electro-conductive agent, poly-tetrafluoro vinylidene resin as a binder, and N-methyl-2-pyrrolidone as a solvent for the binder were stirred to be mixed by a homogenizer to obtain a slurry active material mixture for a positive electrode. One side of an electric collector made of aluminum foil was coated with this slurry mixture using a slot die coater, and thereafter dried at  $130^\circ\text{C}$  in an oven to remove the solvent. The other side of the electric collector was coated therewith, and thereafter the solvent was removed by the same manner as above in order to coat both sides of the electric collector with active material mixture. Then, it was pressed with a roller press and heated in a vacuum oven to remove the moisture to obtain a positive electrode.

On the other hand, a negative electrode was made in such a manner that carbon powder capable of electro-chemically occluding and releasing lithium ions, styrene-butadiene rubber type resin and ethyl acetate was stirred to be mixed by a homogenizer to obtain a slurry active material mixture. This slurry active material mixture coated on one side of an electric collector made of copper foil using a slot die coater, and thereafter it was dried in an oven at  $130^\circ\text{C}$  to remove the solvent. The other side of the electric collector was also coated therewith and the solvent was removed in the same manner as above. The electric collector with the active material mixture on both sides thereof thus obtained was then subjected to a heat treatment so as to cure styrene butadiene rubber type resin, and then pressed with a heated roller press and was then dried to remove the moisture to obtain a negative electrode.

#### 1. Evaluation of cycle characteristics

The positive electrode and the negative electrode thus obtained were stacked one upon another through a separator made of micro porous resin film which has a three-dimensional (sponge-like) structured polyolefine resins (polyethylene, polypropylene or a copolymer thereof). And it was wound to form a spiral electrode assembly. The spiral electrode assembly thus obtained was put in a tubular container made of stainless steel. The opening of the container was closed with a cover, and after an electrolyte was poured, to obtain a sealed lithium secondary battery of AA-size with 500 mAh rated capacity.

In the course of manufacturing a lot of the foregoing batteries, the batteries were poured with respective electrolytes prepared by dissolving  $\text{LiPF}_6$  as a solute in the respective whole solvents for the electrolytes corresponding to examples A - AG, comparative example A and conventional examples A - C having the respective compositions in the volume ratios of component solvents, when measured at  $25^\circ\text{C}$  as shown in Table 1, so as to become the concentration of the solute 1 mol/l.

In Table 1, [A] represents the volume rate of the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure expressions II and III occupied in the whole solvent at temperature of  $25^\circ\text{C}$ . [B] represents the volume rate of other solvents than the organic solvents indicated by structure expressions I, II and III occupied in the whole solvent at a temperature of  $25^\circ\text{C}$ . [A1] represents the volume rate of the organic solvent indicated by structure expression I occupied in the mixture solvent of the organic solvents indicated by structure expressions I, II and III at a temperature of  $25^\circ\text{C}$ . [A2] represents the volume rate of one kind or two selected from the group of the organic solvents indicated by structure expressions II and III occupied in the mixture solvent of the organic solvents indicated by structure expressions I, II and III at a temperature of  $25^\circ\text{C}$ . [II] represents the volume rate of the organic solvent indicated by structure expression II

occupied in the mixture solvent indicated by structure expressions II and III at a temperature of 25°C. [III] represents the volume rate of the organic solvent indicated by structure expression III occupied in the mixture solvent indicated by structure expressions II and III at a temperature of 25°C. Further, PC stands for propylene carbonate and MEC stands for methyl ethyl carbonate.

TABLE 1

	Composition of solvents for electrolytes (volume %)							
	[A]					[B]		
	Composition of [A]					Composition of [B]		
	[A1]	[A2]	Composition of [A2]					
			[II]	[III]	PC	MEC		
Example A	50	50	50	100	0	50	100	0
Example B	60	50	50	100	0	40	100	0
Example C	70	50	50	100	0	30	100	0
Example D	80	50	50	100	0	20	100	0
Example E	90	50	50	100	0	10	100	0
Example F	100	50	50	100	0	0	-	-
Example G	50	50	50	0	100	50	0	100
Example H	60	50	50	0	100	40	0	100
Example I	70	50	50	0	100	30	0	100
Example J	80	50	50	0	100	20	0	100
Example K	90	50	50	0	100	10	0	100
Example L	100	50	50	0	100	0	-	-
Example M	50	50	50	50	50	50	50	50
Example N	60	50	50	50	50	40	50	50
Example O	70	50	50	50	50	30	50	50
Example P	80	50	50	50	50	20	50	50
Example Q	90	50	50	50	50	10	50	50
Example R	100	50	50	50	50	0	-	-
Example S	100	30	70	100	0	0	-	-
Example T	100	35	65	100	0	0	-	-
Example U	100	55	45	100	0	0	-	-
Example V	100	65	35	100	0	0	-	-
Example W	100	70	30	100	0	0	-	-
Example X	80	30	70	0	100	20	50	50
Example Y	80	35	65	0	100	20	50	50
Example Z	80	55	45	0	100	20	50	50
Example AA	80	65	35	0	100	20	50	50
Example AB	80	70	30	0	100	20	50	50
Example AC	70	30	70	50	50	30	50	50
Example AD	70	35	65	50	50	30	50	50
Example AE	70	55	45	50	50	30	50	50
Example AF	70	65	35	50	50	30	50	50
Example AG	70	70	30	50	50	30	50	50
Comparative example A	50	100	0	-	-	50	0	100

to be continued

TABLE 1 continued

TABLE I	continued		Composition of solvents for electrolytes (volume %)					
	[A]					[B]		
	Composition of [A]					composition of [B]		
	[A1]	[A2]	Composition of [A2]					
			[II]	[III]	PC	MEC		
Conventional example A	0	-	-	-	-	100	50	50
Conventional example B	50	0	100	100	0	50	100	0
Conventional example C	50	0	100	0	100	50	100	0

Each of the batteries thus manufactured was charged and discharged repeatedly 10 cycles for the initial activation in such a manner that it was charged with a current density of 0.2CmA, at a temperature of 25°C until the battery voltage reached 4.2V, and after allowed to stand for ten minutes, it was discharged with the same current as above until the battery voltage became 2.75V, and it was then allowed to stand for ten minutes, and the same charging as above was carried out again. Thereafter, for measuring the cycle characteristics, a life test was carried out for each of the batteries in such a manner that it was charged with a current of 0.2CmA, at a temperature of 25°C, until the battery voltage reached 4.2V, and after it was allowed to stand for ten minutes, it was discharged with a current of 0.7CmA until the battery voltage became 2.75V, and after, it was allowed to stand for ten minutes, the same charging was carried out again. Here, the battery life is determined by the number of charge / discharge cycles counted until a discharge capacity of the each battery has been reduced to 70 % of the discharge capacity thereof at the first cycle in the life test. The result thereof is shown in Table 2 below.

TABLE 2

	Battery life (cycle)		Battery life (cycle)
Example A	388	Example T	547
Example B	432	Example U	576
Example C	478	Example V	532
Example D	547	Example W	528
Example E	591	Example X	500
Example F	589	Example Y	512
Example G	368	Example Z	538
Example H	399	Example AA	535
Example I	444	Example AB	421
Example J	532	Example AC	392
Example K	544	Example AD	434
Example L	547	Example AE	428
Example M	373	Example AF	409
Example N	411	Example AG	367
Example O	427	Comparative example A	323
Example P	502	Conventional example A	286
Example Q	531	Conventional example B	345
Example R	575	Conventional example C	307
Example S	523		

Examples A - AG which are the batteries made according to the present invention exhibit longer in life as compared with conventional examples A - C which are conventionally made batteries and with comparative example A which is a battery made for comparison. Accordingly, it has been found therefrom that the electrolytes according to the present invention are effective in improving the cycle characteristics of the lithium secondary batteries.

Furthermore, especially, examples D - F, examples J - L and examples P - R, among examples A - R, in which the volume rate of the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure expression II and structure expression III are 80% or more of the whole solvent under environmental condition of 25°C, exhibit more than 500 cycles which prove longer life than the other examples each in which the volume rate thereof is less than 80%. Also, it has been found therefrom that if the volume rate of the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure expression II and structure expression III is 80% or more of the whole solvent under environmental condition of 25°C, it is much effective in improvement in the cycle characteristics of the lithium secondary batteries.

## 2. Evaluation of discharge capacity

The above-mentioned positive electrode and negative electrode were stacked one upon another through a separator made of a microporous resin film having a three dimensional sponge-like structure of such a polyolefine resin as polyethylene, polypropylene or a copolymer thereof, and it was wound to form a spiral electrode assembly. The spiral electrode assembly thus obtained was put in a tubular container made of stainless steel. The opening of the container was closed with a cover, after an electrolyte was poured, to obtain a lithium secondary battery of AA-size.

In the course of manufacturing a lot of the foregoing batteries, the batteries were poured with respective electrolytes prepared by dissolving  $\text{LiPF}_6$  as a solute in the respective whole solvent for the electrolyte corresponding to examples F, L and R-AG and conventional example A having the respective compositions in the volume ratios of the component solvents when measured at 25°C as shown in Table 1, so as to become the concentration of the solute 1



mol/l.

Each of the batteries thus manufactured was charged and discharged repeatedly 10 cycles for the initial activation in such a manner that it was charged with a current of 0.2CmA, at a temperature of 25°C until the battery voltage reached 4.2V, and after allowed to stand for ten minutes, it was discharged with the same current as above until the battery voltage became 2.75V, and after it was allowed to stand for ten minutes, the same charging as above was carried out again. Thereafter, a discharge capacity test was carried out for each battery in such a manner that it was charged with a current of 0.2CmA, at a temperature of 25°C, until the battery voltage reached 4.2V, and after it was allowed to stand for ten minutes, it was discharged with a current of 1CmA until the battery voltage became 2.75V. The result of measuring the discharge capacity of each battery is shown in Table 3 below. Those lithium secondary batteries were so designed as to obtain the same capacity by including the same amounts of the active materials in the positive and negative electrodes.

TABLE 3

	Discharge Capacity (mAh)		Discharge Capacity (mAh)
Example F	532	Example Z	513
Example L	524	Example AA	501
Example R	500	Example AB	466
Example S	468	Example AC	483
Example T	519	Example AD	510
Example U	507	Example AE	507
Example V	500	Example AF	503
Example W	466	Example AG	471
Example X	471	Conventional Example A	467
Example Y	512		

It has been found therefrom that examples F, L and R-AG, which are the batteries made according to the present invention, are all provided with equal or more discharge capacity to or than the conventional batteries and enough to be acceptable as a practical use, in spite of such a large discharge current that is 1CA, and especially, examples F, L, R, T - V, Y-AA and AD - AF, in which the volume rate of the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure expressions II and III is more 80% or more of the whole solvent, when measured under environmental temperature of 25°C, and the volume rate of the organic solvent indicated by structure expression I occupied in the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure expressions II and III is in the range of 35 - 65 % when measured under environmental temperature of 25°C, exhibit such a large discharge capacity that is more than 500mAh, and thus there can be obtained lithium secondary batteries which are excellent also in the high-rate discharge characteristics, in addition to the above-mentioned much excellent cycle characteristics.

### 3. Evaluation of self-extinguishing characteristics

The following test was carried out for confirming self-extinguish characteristics of the electrolytes used for the batteries of the present invention.

Various electrolytes were prepared by dissolving LiPF<sub>6</sub> as a solute in the respective whole solvent corresponding to the example AH - ER having the respective composition in the volume ratios of the component solvents at 25°C as shown in Table 4, so as to become the concentration of the solute 1 mol/l. Here, in Table 4, [A], [B], [A1], [A2], [I] and [III] respectively represent the same as in Table 1. PC stands for propylene carbonate and MEC stands for methyl ethyl carbonate.

TABLE 4

	Composition of solvents for electrolytes (volume %)						
	[A]					[B]	
	Composition of [A]						
	[A1]	[A2]					
		Composition of [A2]					
					[II]	[III]	
Example AH	65	35	65	100	0	35	PC
Example AI	70	35	65	100	0	30	PC
Example AJ	80	35	65	100	0	20	PC
Example AK	90	35	65	100	0	10	PC

to be continued

TABLE 4 continued

TABLE 4

continued

	Composition of solvents for electrolytes (volume %)						
	[A]					[B]	
	Composition of [A]					kind of solvent	
	[A1]	[A2]					
		Composition of [A2]					
			[II]	[III]			
Example AL	65	35	65	0	100	35	PC
Example AM	70	35	65	0	100	30	PC
Example AN	80	35	65	0	100	20	PC
Example AO	90	35	65	0	100	10	PC
Example AP	100	35	65	0	100	0	-
Example AQ	65	35	65	50	50	35	PC
Example AR	70	35	65	50	50	30	PC
Example AS	80	35	65	50	50	20	PC
Example AT	90	35	65	50	50	10	PC
Example AU	100	35	65	50	50	0	-
Example AV	65	35	65	100	0	35	MEC
Example AW	70	35	65	100	0	30	MEC
Example AX	80	35	65	100	0	20	MEC
Example AY	90	35	65	100	0	10	MEC
Example AZ	65	35	65	0	100	35	MEC
Example BA	70	35	65	0	100	30	MEC
Example BB	80	35	65	0	100	20	MEC
Example BC	65	35	65	50	50	35	MEC
Example BD	70	35	65	50	50	30	MEC
Example BE	80	35	65	50	50	20	MEC
Example BF	100	35	65	50	50	0	-
Example BG	65	50	50	100	0	35	PC
Example BH	65	50	50	0	100	35	PC
Example BI	70	50	50	0	100	30	PC
Example BJ	80	50	50	0	100	20	PC
Example BK	90	50	50	0	100	10	PC
Example BL	65	50	50	50	50	35	PC
Example BM	70	50	50	50	50	30	PC
Example BN	80	50	50	50	50	20	PC
Example BO	90	50	50	50	50	10	PC
Example BP	65	50	50	100	0	35	MEC
Example BQ	70	50	50	100	0	30	MEC
Example BR	80	50	50	100	0	20	MEC
Example BS	90	50	50	100	0	10	MEC
Example BT	65	50	50	0	100	35	MEC
Example BU	65	50	50	50	50	35	MEC
Example BV	70	50	50	50	50	30	MEC

to be continued

TABLE 4 continued

TABLE 4

Continued

	Composition of solvents for electrolytes (volume %)						
	[A]					[B]	
	Composition of [A]					kind of solvent	
	[A1]	[A2]					
		Composition of [A2]					
II]		III]					
Example BW	80	50	50	50	50	20	MEC
Example BX	90	50	50	50	50	10	MEC
Example BY	65	60	40	100	0	35	PC
Example BZ	70	60	40	100	0	30	PC
Example CA	80	60	40	100	0	20	PC
Example CB	90	60	40	100	0	10	PC
Example CC	100	60	40	100	0	0	-
Example CD	65	60	40	0	100	35	PC
Example CE	70	60	40	0	100	30	PC
Example CF	80	60	40	0	100	20	PC
Example CG	90	60	40	0	100	10	PC
Example CH	100	60	40	0	100	0	-
Example CI	65	60	40	50	50	35	PC
Example CJ	70	60	40	50	50	30	PC
Example CK	80	60	40	50	50	20	PC
Example CL	90	60	40	50	50	10	PC
Example CM	100	60	40	50	50	0	-
Example CN	65	60	40	100	0	35	MEC
Example CO	70	60	40	100	0	30	MEC
Example CP	80	60	40	100	0	20	MEC
Example CQ	90	60	40	100	0	10	MEC
Example CR	65	60	40	0	100	35	MEC
Example CS	70	60	40	0	100	30	MEC
Example CT	80	60	40	0	100	20	MEC
Example CU	90	60	40	0	100	10	MEC
Example CV	65	60	40	50	50	35	MEC
Example CW	70	60	40	50	50	30	MEC
Example CX	80	60	40	50	50	20	MEC
Example CY	90	60	40	50	50	10	MEC
Example CZ	65	80	20	100	0	35	PC
Example DA	70	80	20	100	0	30	PC
Example DB	80	80	20	100	0	20	PC
Example DC	90	80	20	100	0	10	PC
Example DD	100	80	20	100	0	0	-
Example DE	65	80	20	0	100	35	PC
Example DF	70	80	20	0	100	30	PC

to be continued

TABLE 4 continued

TABLE 4 continued

	Composition of solvents for electrolytes (volume %)						
	[A]					[B]	
	Composition of [A]					kind of solvent	
	[A1]	[A2]					
		Composition of [A2]					
			(II)	(III)			
Example DG	80	80	20	0	100	20	PC
Example DH	90	80	20	0	100	10	PC
Example DI	100	80	20	0	100	0	-
Example DJ	65	80	20	50	50	35	PC
Example DK	70	80	20	50	50	30	PC
Example DL	80	80	20	50	50	20	PC
Example DM	90	80	20	50	50	10	PC
Example DN	100	80	20	50	50	0	-
Example DO	65	80	20	100	0	35	MEC
Example DP	70	80	20	100	0	30	MEC
Example DQ	80	80	20	100	0	20	MEC
Example DR	90	80	20	100	0	10	MEC
Example DS	65	80	20	0	100	35	MEC
Example DT	70	80	20	0	100	30	MEC
Example DU	80	80	20	0	100	20	MEC
Example DV	90	80	20	0	100	10	MEC
Example DW	65	80	20	50	50	35	MEC
Example DX	70	80	20	50	50	30	MEC
Example DY	80	80	20	50	50	20	MEC
Example DZ	90	80	20	50	50	10	MEC
Example EA	60	35	65	100	0	40	PC
Example EB	60	35	65	0	100	40	PC
Example EC	60	35	65	50	50	40	PC
Example ED	60	35	65	100	0	40	MEC
Example EE	60	35	65	0	100	40	MEC
Example EF	60	35	65	50	50	40	MEC
Example EG	65	30	70	100	0	35	PC
Example EH	65	30	70	0	100	35	PC
Example EI	65	30	70	50	50	35	PC
Example EJ	65	30	70	100	0	35	MEC
Example EK	65	30	70	0	100	35	MEC
Example EL	65	30	70	50	50	35	MEC
Example EM	60	30	70	100	0	40	PC
Example EN	60	30	70	0	100	40	PC
Example EO	60	30	70	50	50	40	PC
Example EP	60	30	70	100	0	40	MEC
Example EQ	60	30	70	0	100	40	MEC
Example ER	60	30	70	50	50	40	MEC

Also, various mixture electrolytes were prepared by dissolving  $\text{LiPF}_6$  as a solute in the respective white solvents for the electrolytes corresponding to examples C, D, E, F, L, R and T, comparative example A, and conventional examples A - C having the respective compositions in the volume ratios of the component solvents as shown in Table 1, so as to adjust the solute concentration to 1 mol/l.

# EP 0 806 804 A1

Self-extinguishing characteristics of each of the electrolytes prepared as above was examined by a test where sheets of paper were immersed in the respective electrolytes to be tested, and were then set fire by a flame of a burner and thereafter the flame was put out. Thus the self-extinguishing characteristics was confirmed by observing as to whether the firing was still continued or discontinued when the flame was put out. The results of self-extinguishing characteristics are shown in Table 5 below.

TABLE 5

	fire continued / discontinued		fire continued / discontinued
Example AH	fire discontinued	Example BI	fire discontinued
Example AI	fire discontinued	Example BJ	fire discontinued
Example AJ	fire discontinued	Example BK	fire discontinued
Example AK	fire discontinued	Example BL	fire discontinued
Example AL	fire discontinued	Example BM	fire discontinued
Example AM	fire discontinued	Example BN	fire discontinued
Example AN	fire discontinued	Example BO	fire discontinued
Example AO	fire discontinued	Example BP	fire discontinued
Example AP	fire discontinued	Example BQ	fire discontinued
Example AQ	fire discontinued	Example BR	fire discontinued
Example AR	fire discontinued	Example BS	fire discontinued
Example AS	fire discontinued	Example BT	fire discontinued
Example AT	fire discontinued	Example BU	fire discontinued
Example AU	fire discontinued	Example BV	fire discontinued
Example AV	fire discontinued	Example BW	fire discontinued
Example AW	fire discontinued	Example BX	fire discontinued
Example AX	fire discontinued	Example BY	fire discontinued
Example AY	fire discontinued	Example BZ	fire discontinued
Example AZ	fire discontinued	Example CA	fire discontinued
Example BA	fire discontinued	Example CB	fire discontinued
Example BB	fire discontinued	Example CC	fire discontinued
Example BC	fire discontinued	Example CD	fire discontinued
Example BD	fire discontinued	Example CE	fire discontinued
Example BE	fire discontinued	Example CF	fire discontinued
Example BF	fire discontinued	Example CG	fire discontinued
Example BG	fire discontinued	Example CH	fire discontinued
Example BH	fire discontinued	Example CI	fire discontinued

to be continued

TABLE 5 continued

	fire continued / discontinued		fire continued / discontinued
Example CJ	fire discontinued	Example DV	fire discontinued
Example CK	fire discontinued	Example DW	fire discontinued
Example CL	fire discontinued	Example DX	fire discontinued
Example CM	fire discontinued	Example DY	fire discontinued
Example CN	fire discontinued	Example DZ	fire discontinued
Example CO	fire discontinued	Example EA	fire continued
Example CP	fire discontinued	Example EB	fire continued
Example CQ	fire discontinued	Example EC	fire continued
Example CR	fire discontinued	Example ED	fire continued
Example CS	fire discontinued	Example EE	fire continued
Example CT	fire discontinued	Example FE	fire continued
Example CU	fire discontinued	Example EG	fire continued
Example CV	fire discontinued	Example EH	fire continued
Example CW	fire discontinued	Example EI	fire continued
Example CX	fire discontinued	Example EJ	fire continued
Example CY	fire discontinued	Example EK	fire continued
Example CZ	fire discontinued	Example EL	fire continued
Example DA	fire discontinued	Example EM	fire continued
Example DB	fire discontinued	Example EN	fire continued
Example DC	fire discontinued	Example EO	fire continued
Example DD	fire discontinued	Example EP	fire continued
Example DE	fire discontinued	Example EQ	fire continued
Example DF	fire discontinued	Example ER	fire continued
Example DG	fire discontinued	Example C	fire discontinued
Example DH	fire discontinued	Example D	fire discontinued
Example DI	fire discontinued	Example E	fire discontinued
Example DJ	fire discontinued	Example F	fire discontinued
Example DK	fire discontinued	Example I	fire discontinued
Example DL	fire discontinued	Example J	fire discontinued
Example DM	fire discontinued	Example K	fire discontinued
Example DN	fire discontinued	Example L	fire discontinued
Example DO	fire discontinued	Example R	fire discontinued
Example DP	fire discontinued	Example T	fire discontinued
Example DQ	fire discontinued	Comparative Example A	fire continued
Example DR	fire discontinued	Conventional Example A	fire continued
Example DS	fire discontinued	Conventional Example B	fire continued
Example DT	fire discontinued	Conventional Example C	fire continued
Example DU	fire discontinued		

As it is obvious from Table 5, while the electrolytes corresponding to conventional examples A - C and comparative example A continued firing even after putting out the burner's flame, the electrolytes corresponding to examples AH - DZ and examples C, D, E, F, L, R and T used for the battery according to the present invention self-extinguished after putting out the burner's flame, and thus their self-extinguishing characteristics have been confirmed. However, it has been also confirmed that the electrolytes corresponding to examples EA-ER have no self-extinguish characteristics, because the firing thereof continued even after putting out the burner's flame. Therefore, it has been concluded that the electrolytes wherein the volume rate of the mixture solvent prepared by mixing the organic solvent indicated by structure expression I with one kind or two selected from the group of the organic solvents indicated by structure

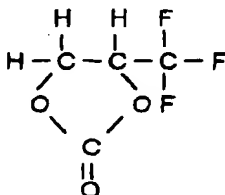
expression II and structure expression III is 65% or more of the whole solvent when measured under environmental temperature of 25°C, and the volume ratio of the organic solvent indicated by structure expression I is 35 % or more of the mixture solvent, when measured under environmental temperature of 25°C, have more improved in self-extinguishing characteristics. Using such a specific range of electrolyte, a lithium secondary battery with high safety characteristics can be supplied.

Thus, according to the present invention, a lithium battery with excellent charge / discharge cycle characteristics can be obtained. Furthermore, by limiting the mixing ratios of the mixture solvent in the electrolyte in the foregoing range, a lithium secondary battery which is provided with high safety and self-extinguishing characteristics in addition to the excellent cycle characteristics can be obtained. In addition, a lithium secondary battery provided also with high-rate discharge characteristics can be obtained.

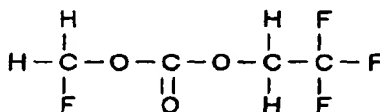
### Claims

1. A lithium secondary battery comprising a negative electrode using as an active material at least one kind selected from the group of metallic lithium, lithium alloys or materials which are capable of electrochemically occluding and releasing lithium ions, a positive electrode using as an active material at least one kind of compounds which are capable of electrochemically occluding and releasing lithium ions, and an organic electrolyte an improvement being that a solvent for the electrolyte is composed mainly of a mixture solvent prepared by mixing an organic solvent indicated by structure expression I, i.e. 4-trifluoromethyl-1,3-dioxolane-2-one, and one kind or two selected from the group of an organic solvent indicated by structure expression II, e.i. 1-trifluoroethylmethyl carbonate, and an organic solvent indicated by structure expression III, i.e. di-1-trifluoroethyl carbonate, as mentioned below.

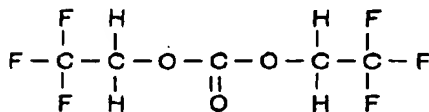
Structure expression I



Structure expression II



Structure expression III



2. A lithium secondary battery according to claim 1, wherein the volume ratio of the mixture solvent occupied in the whole solvent for the organic electrolyte is 65% or more under environmental temperature of 25°C, and the volume



rate of the organic solvent indicated by the structure expression I occupied in the mixture solvent is 35% or more under environmental temperature of 25°C.

- 5
3. A lithium secondary battery according to claim 1 or claim 2, wherein the volume rate of the mixture solvent occupied in the whole solvent for the organic electrolyte is 80% or more under environmental temperature of 25°C.
- 10
4. A lithium secondary battery according to claim 1, claim 2, or claim 3, wherein the volume rate of the mixture solvent occupied in the whole solvent for the organic electrolyte is 80% or more under environmental temperature of 25°C, and the volume rate of the organic solvent indicated by structure expression I occupied in the mixture solvent is 35 - 65% under environmental temperature of 25°C.
- 15
- 20
- 25
- 30
- 35
- 40
- 45
- 50
- 55



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 97 10 7475

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	PATENT ABSTRACTS OF JAPAN vol. 096, no. 006, 28 June 1996 & JP 08 037025 A (JAPAN ENERGY CORP), 6 February 1996, * abstract *	1	H01M10/40
A	EP 0 599 534 A (MITSUI PETROCHEMICAL IND ;SONY CORP (JP)) 1 June 1994 * table 1, compound J * * claims 1,2 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 August 1997	Examiner Andrews, M
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p>			

EPO FORM 1503 01.82 (P04 C01)



Creation date: 02-06-2004  
Indexing Officer: KTRUONG1 - KHANH TRUONG  
Team: OIPEBackFileIndexing  
Dossier: 09879753

Legal Date: 05-22-2003

No.	Doccode	Number of pages
1	SRNT	1

Total number of pages: 1

Remarks:

Order of re-scan issued on .....